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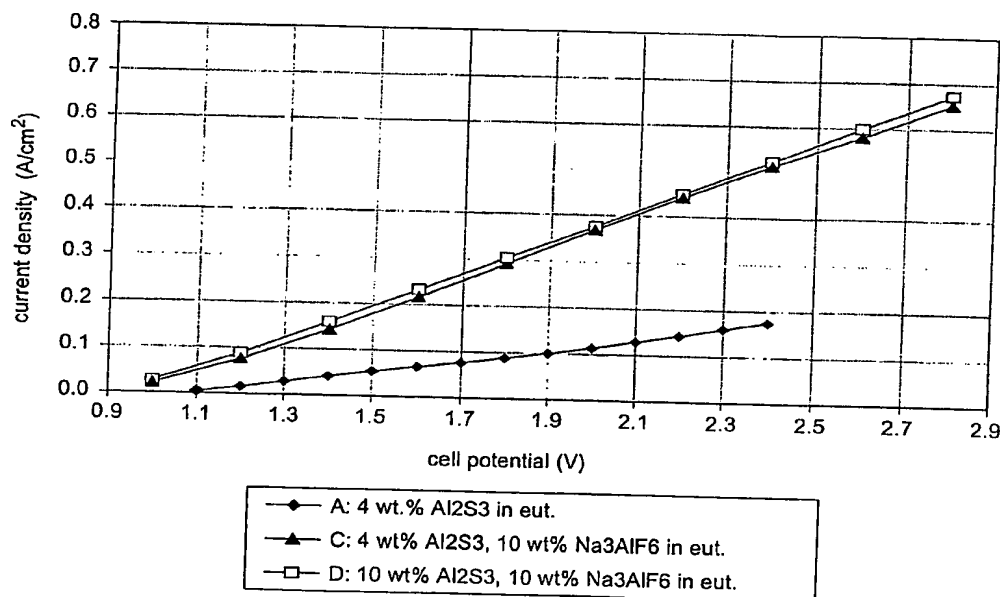
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(54) Title: **PROCESS FOR THE ELECTROLYSIS OF ALUMINIUMSULFIDE**



(57) Abstract: Process for the electrolysis of Al_2S_3 , using a bath of molten salt, preferably a bath of molten chloride salt, in which Al_2S_3 is dissolved characterised in that measures are taken to improve the electrical conductivity of the bath, so as to enable an increase in the current density in the bath.

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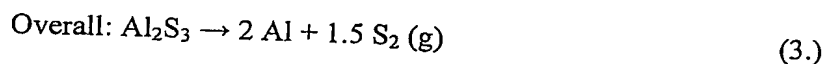
PROCESS FOR THE ELECTROLYSIS OF ALUMINIUMSULFIDE

5 The invention relates to a process for the electrolysis of Al_2S_3 , using a bath of molten salt, preferably a bath of molten chloride salt, in which Al_2S_3 is dissolved.

The most commonly used method for the production of aluminium from aluminium ore is the Hall-Héroult process.

10 Primary aluminum production via electrolysis in the Hall-Héroult process consumes about 13-15 MWh of electrical energy per tonne of aluminum. The anodes are consumed during the process and have to be changed periodically. In addition, the Hall-Héroult process gives rise to green house emissions such as CF_4 and C_2F_6 , which should be removed from the off-gas in compliance with environmental legislation.

15 In an alternative process, aluminium oxide is converted in a sulfidation step into aluminium sulfide Al_2S_3 by a reaction with carbonsulfide CS_2 . A more detailed description of the alternative process, also referred to as Compact Aluminium Production Process or CAPP or more general as sulfide process, is given in patent application WO/00/37691 the content of which is deemed to be included in this description by this reference. The aluminum metal can be extracted from Al_2S_3 by
20 electrolysis, producing sulfur gas at the anode, preferably a graphite anode. The sulfur gas will be collected and recycled to produce CS_2 , which is used in the sulfidation step, which is of particular advantage in combination with the CAPP-process. The simplified reactions (assuming no complexions) of the electrolysis process are:



25 By-products of the Hall-Héroult process such as fluoride off-gases as well as spent pot linings will not be produced, since the electrolyte is basically composed of chlorides.

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Figure 1 shows the decomposition potential of various aluminium compounds to produce aluminium by electrolysis and shows immediately that the electrolysis of Al_2S_3 is very advantageous with regard to energy consumption, i.e. it has the lowest decomposition potential. The first bar is a theoretical value for comparison. The second bar represents a process wherein Al_2O_3 is converted into AlCl_3 which is decomposed. The fourth bar represents the alternative sulfide process and the third bar represents the actual Hall-Héroult process. The theoretical value of the decomposition potential is determined by:

$$E^0 = -\frac{\Delta G^0}{nF}, \text{ whereas}$$

E^0 = the decomposition potential

ΔG^0 = the Gibbs free energy (4.)

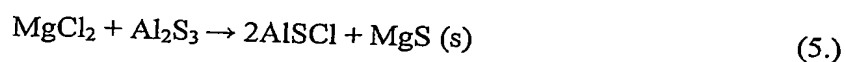
n = the valency of the ion (3 for aluminium)

F = Faraday's constant

A problem with the sulfide process is the low current density that can be achieved in the known molten chloride bath.

The eutectic composition of a MgCl_2 - NaCl - KCl mixture (50-30-20 mole %) has been proposed previously as an appropriate electrolyte for the electrolyses of Al_2S_3 (see N.Q.Minh, R.O. Loutfy, N.P.Yao, "The Electrolysis of Al_2S_3 in AlCl_3 - MgCl_2 - NaCl - KCl Melts", J.Appl. Electrochem, Vol 12, 1982, 653-658; R.O. Loutfy, N.Q. Ming, C. Hsu, N.P. Yao, "Potential Energy Savings in the Production of Aluminium: Aluminium Sulfide Route", Chemical Metallurgy – A Tribute To Carl Wagner, Proc. Of Symp. on Metallurgical Thermodynamics and Electrochemistry at the 110th AIME annual meeting, N.A. Gokcen, Ed., Chicago, Febr. 1981, The Metallurgical Society of AIME, New York, 1981; N.Q. Mingh, R.O. Loutfy, N.P. Yao, "The Electrochemical Behaviour of Al_2S_3 in Molten MgCl_2 - NaCl - KCl Eutectic", J. Electroanal. Chem. Vol. 131, 198, 229-242).

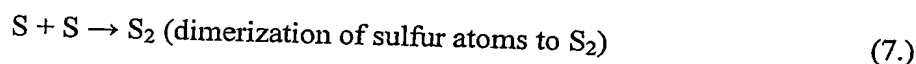
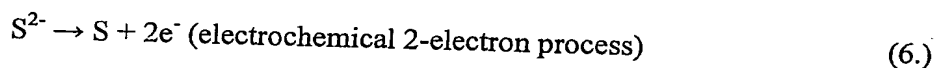
It was thought that the limiting factor in the achievable current density in the bath of molten chloride salt is the solubility of Al_2S_3 . The solubility was enhanced by the use of MgCl_2 which was thought to increase the solubility according to the reaction.



A limiting current density of 0,3 A/cm² at the saturation solubility of Al₂S₃ (≈ 3 wt %) and of 0,2 A/cm² in the MgCl₂-NaCl-KCl eutectic composition containing about 2 wt % Al₂S₃ was measured.

5 The current efficiency, i.e. the percentage of the current that is actually used for the electrolysis was determined to be about 80 % at a current density of 0,2 A/cm², a cell potential of about 1,5 V and an interelectrode gap between anode and cathode of 3 cm.

10 It is reported in literature that electrochemical studies of the electrolysis of Al₂S₃ in a chloride melt showed that the reduction of Al-ions at a graphite electrode is a diffusion controlled process and proceeds via a reversible, 3-electron charge transfer. The oxidation of S-ions in the chloride electrolyte should be a reversible diffusion controlled process proceeding via a mechanism based on two steps:

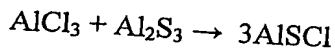


15 The normal current density at which the Hall-Héroult process is carried out is about 0,8 A/cm². The achievable current density in the electrolysis of Al₂S₃ in a eutectic MgCl₂-NaCl-KCl bath is about 0,3 A/cm². This means that the cell area, when applying the sulfide process should be about three times larger than required for the Hall-Héroult process. This makes the sulfide process not an attractive alternative despite the drawbacks associated with the Hall-Héroult process.

20 Because the limiting current densities found are too low to compete with the Hall-Héroult process, where about 0.8 A·cm⁻² is employed, the addition of fluxes to the melt was considered to increase the solubility of Al₂S₃ and to increase the activity of both Al and S in the melt.

25 It is known that increasing the acidity of the bath of molten salt has a beneficial effect on the solubility of Al₂S₃. The addition of AlCl₃ results in a more acidic melt and should favour the solubility. However, due to the high vapour pressure of AlCl₃ (boiling point 447 °C) additions to the molten salt melt are limited because of

volatilization. The addition of 5 – 10 wt % Al_2S_3 increases the solubility of AlCl_3 up to a maximum of 5 – 7 wt % according to the following reaction.



The addition of AlCl_3 allows current densities of up to 2 A/cm^2 , but the use of AlCl_3 is not a viable alternative. Even though the eutectic temperature of a MgCl_2 -
5 NaCl-KCl mixture is relatively low, the high vapour pressure of AlCl_3 causes a considerable amount of AlCl_3 to volatilise.

In prior publications AlCl_3 was used to enhance the electrowinning process. Since AlCl_3 is readily volatilized from the melt and has to be separated from sulfur
downstream to recycle it to the electrowinning process, it was discarded as being
10 impractical.

It is an object of the present invention to provide a process for the electrolysis of Al_2S_3 which allows a high current density, preferably comparable with or higher than the current density achieved in the Hall-Héroult process.

It is further object to the present invention to provide a process for the
15 electrolysis of Al_2S_3 which allows a high current density without the use of AlCl_3 .

It is another object of the invention to provide a process for the electrolysis of Al_2S_3 in which virtually all of the sulfur can be recycled to form new Al_2S_3 from Al_2O_3 .

These and further objects are reached in a process for the electrolysis of Al_2S_3 using a bath of molten salt, preferably a bath of molten chloride salt, in which Al_2S_3 is
20 dissolved which is characterised in that measures are taken to improve the electrical conductivity of the bath, so as to enable an increase in the current density in the bath.

Different from what is suggested in the prior art, the present inventors have found that the solubility of Al_2S_3 in a bath of molten salt having an appropriate composition is not the limiting factor in the achievable current density. The cell
25 potential of an electrolysis cell is built up of thermodynamic, kinetic (activation potential and mass transfer limitations) and ohmic contributions. The inventors have taken a different approach and found a nearly linear relationship between current density and cell potential which indicates that the electrolysis process, at least above a

minimum concentration of dissolved Al_2S_3 , is not diffusion controlled, but has ohmic limitations. Then, as observed by the present inventors, an increased solubility of Al_2S_3 does not result in a substantial enhancement of the cell performance. The relationship between cell potential and current density is nearly linear, which means that this relation is determined by an ohmic relation. Consequently the allowable current density can be increased by improving the electrical conductivity of the bath.

Preferably the conductivity is improved in an embodiment of the invention in which the measures comprise adding an additive to the bath.

The additives are selected so as to increase the overall electrical conductivity in the bath of molten salt. As an additional effect the additives may increase the activity of both aluminium and sulfur and also the solubility of Al_2S_3 . As described above AlCl_3 is not a preferred addition.

A preferred embodiment of the process according to the invention is characterised in that the additive comprises, preferably mainly consists of a fluoride compound.

This embodiment is based on the insight that the amount of fluoride has a positive effect on the electrolysis process resulting from a higher activity of AlF_n^{m-} than AlS^+ species. Also, as complexing of aluminium with fluor is favoured over complexing of aluminium with sulfur, the concentration of sulfur ions is higher when fluoride is added, favouring the anodic reaction.

A further preferred embodiment of the process according to the invention is characterised in that the fluoride compound is cryolite.

It has been found that addition of cryolite shows a larger improvement of the conductivity than the addition of other fluorides such as NaF , although the specific conductivity of NaF is much higher.

Another advantages of adding cryolite, is that cryolite has a high melting point (1012 °C and therefore much higher than the boiling point of AlCl_3) and volatilization of cryolite at the normal operating temperature of the electrolysis cell is assumed to be negligible.

It can be argued that adding fluoride is not desirable, since this results in fluoride emissions. However, the required amount of cryolite is relatively small and operating temperatures are only about 700 °C, compared to about 950 °C for the conventional Hall-Héroult process. Thus the vapor pressure of fluorides will be very low. The anode effect can be avoided, because sulfur reacts at the anode. As non-consumable anodes can be used, the electrowinning can be carried out in a closed system, providing improved off-gas capturing.

Another embodiment of the process according to the inventors is characterised in that the concentration of the cryolite is in the range of 5 – 30 wt %, preferably 7 – 15 wt %, more preferably about 10 wt %. Test have shown that relatively low concentrations of cryolite are sufficient to obtain the desired increase in conductivity with an optimum concentration of about 10 wt %.

From the relationship between current density and cell potential in an electrolysis cell containing a bath of molten salt, and from the effect of cryolite and NaF addition, it was concluded that the beneficial effect of the addition of fluoride containing additives cannot solely be ascribed to the increased specific conductivity of the melt.

It was concluded that the process according to the invention is also improved in a embodiment which is characterised in that the measures comprise enhancing the effective area of an anode extending into the bath by reducing the amount and/or size of gas bubbles covering the anode.

The following observations have been made that justify the conclusion that the beneficial effect of the addition of fluoride containing fluxes cannot solely be ascribed to the increased specific conductivity of the melt:

- The slope of the current density vs. cell potential relationship increases by almost a factor 3 on the addition of cryolite to the MgCl_2 -NaCl-KCl eutectic, which is much more than can be expected from the increased conductivity.
- The addition of 10 wt.% cryolite shows a larger improvement of the apparent conductivity than the addition of NaF, although the specific conductivity of NaF is much higher.

- There seems to be an optimum amount of fluoride, or fluoride to aluminium ratio, in the electrolyte.

The explanation proposed is that a significant portion of the ohmic drop is not related to the bath of molten salt itself but due to the gas bubbles at the anode, since they have virtually zero conductivity and reduce the available anode surface. In literature it has been shown that the main contribution to the cell potential is due to the anodic reaction. It has been determined previously for chlorine evolution in a chloride melt that the apparent conductivity was only about 40% of the specific conductivity of the electrolyte, due to gas bubbles. Chlorine bubbles have the tendency to grow and stick to the anode and the overpotential could be interpreted as an ohmic potential drop in a surface layer at the anode. The same reasoning may apply as regards the evolution of sulfur gas in a chloride melt.

It is expected that the quantity of sulfur gas formed at the anode is not changed by the addition of cryolite, but that gas bubbles adhere less strongly or are easier removed from the anode, so that a layer of gas bubbles is less dense.

Therefore, a hypothesis can be postulated that on the addition of fluoride; a complex ion is formed, changing interfacial tension at the anode, resulting in different characteristics of the sulfuric bubble layer at the anode surface area, significantly reducing the ohmic drop as well as the energy consumption.

A preferred embodiment of the process according to the invention is characterised in that the bath of molten salt mainly comprises alkali metal chlorides, preferably KCl and NaCl.

From the prior art it is known to use a bath of molten chloride salts comprising NaCl, KCl and $MgCl_2$. In particular the last compound is added to increase the solubility of Al_2S_3 since the solubility in a bath of molten NaCl and KCl is negligible. However the present inventors have realised that addition of suitable additives like cryolite increases the solubility of Al_2S_3 in the bath of molten alkali metal chlorides to a level at which the solubility is no longer the limiting factor in the electrolysis process but the conductivity. This has opened the way to a simple and more environmentally friendly bath.

A particular advantageous embodiment of the process according to the invention is characterised in that the bath of molten metal is substantially free of earth alkaline chlorides.

5

It was found that a sufficient solubility in combination with a high conductivity can also be obtained in a bath of molten salt which is substantially free of earth alkaline chlorides, in particular free of MgCl_2 , in particular when the above mentioned fluoride additions are made. This is of particular interest since earth alkalines like Mg react with the sulfur in the bath and form solid MgS hereby consuming sulfur. Basically the sulfide process in the form of CAPP process does not consume sulfur, since all sulfur can be recycled.

Through the creation of MgS a considerable amount of sulfur is removed from the sulfur recycle loop, which makes supply of sulfur necessary at extra costs. Moreover, formation of MgS will lead to a substantial waste stream of environmentally unfriendly material, which needs to be recycled. Finally, formation of MgS will impede cell operation, and make regular cleaning of the cell necessary, which conflicts with the closed cell concept and leads to poor working conditions. Similar problems are to be expected in case other earth alkaline chlorides, such as CaCl_2 , are used. Therefore, preferably, the bath of molten salt is substantially free of earth alkaline chlorides.

In a further preferred embodiment of the process according to the invention the electrolysis is carried out at a bath temperature of between 600°C and 850°C , preferably between 700°C and 800°C .

In the known process MgCl_2 is added to the bath of molten salt to increase the solubility of Al_2O_3 and to lower the melting temperature of the bath so that AlCl_3 can be added to increase solubility.

By deleting MgCl_2 and adding cryolite, the melting temperature of the bath is increased, but that is acceptable since the melting point of cryolite is much higher than the proposed bath temperatures. Further it has to be recognised that the melting temperature of the NaCl-KCl eutect is still substantially lower than proposed bath temperature.

A still further preferred embodiment of the process according to the invention, is characterised in that the electrolysis is carried out in a multi-polar electrolysis cell.

Because of operation with non-consumable anodes, the interelectrode gap can be reduced and kept constant and a multi-polar cell operation is possible, which will
5 increase productivity, reduce energy consumption and reduce capital costs

The invention will now be further explained and elucidated with reference to the drawing in which

Fig. 1 shows the decomposition potential of aluminium compounds to produce aluminium by electrolysis.

10 Fig. 2 shows a schematic view of an experimental electrolysis cell.

Fig. 3 shows a plot of cathodic current density as a function of the cell potential for the electrolysis of aluminium from Al_2S_3 in a MgCl_2 - NaCl - KCl electrolyte of 50-30-20 mole % at 725 °C using cryolite as an additive (flux).

15 Fig. 4 shows a plot of cathodic current density as a functions of the cell potential for the electrolysis of aluminium from 4 wt % Al_2S_3 in a MgCl_2 - NaCl - KCl electrolyte of 50-30-20 mole % at 725 °C using different amounts of cryolite as an additive (flux).

20 Fig. 5 shows a plot of the cathodic current density as a function of the cell potential for the electrolysis of aluminium from 4 wt % Al_2S_3 in a MgCl_2 - NaCl - KCl electrolyte of 50-30-20 mole % of 725 °C using NaF as an additive (flux).

Fig. 1 has been described above.

The electrolysis of aluminum from aluminum sulfide is carried out in a two electrode system. A schematic view of the experimental cell is depicted in Figure 2. The cathode is a pool of molten aluminum (1) (effective area 8.1 cm²), which is
25 polarized by a graphite block (2) connected by a rod of stainless steel (3) shielded by a quartz tube (4). The anode is constructed of a graphite block (5) of 1 cm², 5 cm high, which is immersed 2 cm into the electrolyte and is connected by a stainless steel rod (7). The interelectrode gap is 2 cm. The anode acts as the reference electrode, thus the cell

potential is measured during the electrolysis. The electrochemical cell is constructed of sintered Al_2O_3 (Alsint) walls (10). The melt is protected by an inert Ar atmosphere. Argon is introduced through inlet (8) and leaves the cell through outlet (9). The cell is externally heated by a 2100W cylindrical furnace equipped with heating elements (not shown). The maximum operating temperature is 1400 °C. The temperature is measured and controlled by type S thermocouples and a control unit (not shown).

The potential is measured with a potentiostat/galvanostat, which was used in combination with a current booster, to enable a high current throughput (20 A range). The electrochemical measurement system is fully computer controlled.

10 Tests as described below were carried out with a MgCl_2 -NaCl-KCl mixture, but the results also apply to a NaCl-KCl mixture.

All chemicals were stored and handled in a glove box, having an argon atmosphere (< 1 ppm H_2O , O_2). KCl, NaCl and NaF were of pro analysis quality. Anhydrous MgCl_2 (98 %), Al_2S_3 (98 %) and Na_3AlF_6 (98 %) were commercially obtained from a supplier. The chloride electrolyte mixture was composed and put in a container in the glove box. This container was then taken out of the glove box and heated to 450 °C while purging HCl gas through the solids and subsequently through the melt to remove all water and oxides. After cooling the container was put back into the glove box. The Al_2S_3 and additives were added at room temperature in the glove box. The electrolysis cell was assembled in the glove box, closed, then transported to the furnace where an Ar flow prevented contact with air. An overview of the salt mixtures used for the experimental program discussed in this paper is given in the table below.

Overview of Experimental Program of the electrolysis of
Al from Al_2S_3 in a MgCl_2 -NaCl-KCl Electrolyte of 50-30-
20 mole% at 725 °C.

<i>Exp.</i>	<i>Al_2S_3</i> (wt. %)	<i>Flux</i>	<i>Amount of flux</i> (wt. %)
A	4	-	-
B	4	-	-
C	4	Na_3AlF_6	10
D	10	Na_3AlF_6	10
E	4	Na_3AlF_6	5
F	4	Na_3AlF_6	15
G	4	Na_3AlF_6	20
H	4	Na_3AlF_6	30
K	4	NaF	10
L	4	NaF	30

Figure 3 shows the major improvement of the electrolysis performance, because of the addition of Na_3AlF_6 . When adding 10 wt.% of Na_3AlF_6 , the electrolyte composition changes to a quaternary mixture of 48-29-19-4 mole% of MgCl_2 -NaCl-KCl- Na_3AlF_6 . The current density is more than 3 times larger at a given cell potential. By linear extrapolation it has been determined that $E = 0.98$ V, which equals the theoretical decomposition potential. This is another indication, that the process is ohmically limited rather than diffusion controlled. The Nernst equation indicates that the activity of Al_2S_3 in a melt with cryolite addition approaches unity. Further increase of the Al_2S_3 concentration in the melt did not produce a significant effect (compare experiments C and D).

Figure 4 depicts a graph showing the influence of the amount of cryolite added to the melt. There seems to be an optimum at about 10 wt.% cryolite addition.

Experimental work has been carried out in order to investigate whether the positive influence of cryolite on the performance of the electrowinning was caused by

the amount fluoride added, or by increasing the amount of Al-ions in the electrolyte. Therefore, NaF was used as a fluxing agent. The addition of 10 wt.% NaF results in a melt composition of 42-25-17-16 mole% MgCl_2 -NaCl-KCl-NaF composition. On an elemental basis, the amount of F in the electrolyte is comparable to the cryolite melt, i.e. 6.4 and 7.6 mole% F respectively. Figure 5 depicts the results of those experiments. Increasing the amount of NaF to 30 wt.% shows a deteriorating cell performance, which again is in agreement with the results of cryolite additions.

The linear current density-cell potential relationships observed from Figure 3 to Figure 5 indicate that the electrolysis process with these high concentrations of dissolved Al_2S_3 is no longer diffusion controlled, but shows ohmic limitations. Then, an increased solubility of Al_2S_3 would not result in a substantial enhancement of the cell performance. This is supported by the experimental results. It is assumed that the addition of Na_3AlF_6 to the melt has a positive effect on the solubility of Al_2S_3 . Therefore, the amount of Al_2S_3 added to the quaternary mixture was increased from 4% to 10% (Exp. C and D in Figure 3). However, this did not improve the cell performance significantly, indicating that diffusion is not the rate limiting step with these relatively high concentrations of Al_2S_3 employed.

At first sight, it can be argued that because of the ohmic control of the process, increasing the conductivity of the melt should result in an increased current density. Since cryolite has a higher conductivity than the chloride eutectic, a better performance is at least to some extent the result of the increased conductivity. When adding 10 wt.% of Na_3AlF_6 , the electrolyte composition changes to a quaternary mixture of 48-29-19-4 mole% of MgCl_2 -NaCl-KCl- Na_3AlF_6 , which can have significantly different properties. However, the slope of the linear relationship increased by almost a factor 3 when cryolite was added, which cannot be attributed to the increased conductivity of the melt only. Furthermore, although the specific conductivity of NaF is the highest of all components, i.e. $4.2 \Omega^{-1} \cdot \text{cm}^{-1}$ at 725 °C, the effect of adding NaF is less pronounced.

As cryolite and NaF additions produce similar effects, it can be argued that the amount of fluoride contributes to the positive effect on the electrolysis process, resulting from a higher activity of AlF_n^{m-} than AlS^+ species. Also, when complexing of Al with F is favoured over complexing with S, the concentration of S-ions is higher when fluoride is added, favoring the anodic reaction.

As described earlier, the major benefit of fluoride additions was found to be an increase in conductivity of the melt, which is most favourably explained in terms of a reduced coverage of the anode by a sulfur gas bubbles layer.

CLAIMS

1. Process for the electrolysis of Al_2S_3 , using a bath of molten salt, preferably a bath of molten chloride salt, in which Al_2S_3 is dissolved characterised in that measures are taken to improve the electrical conductivity of the bath, so as to enable an increase in the current density in the bath.
2. Process according to claim 1 characterised in that the measures comprise adding an additive to the bath.
3. Process according to claim 2 characterised in that the additive comprises, preferably mainly consists of a fluoride compound.
4. Process according to claim 3 characterised in that the fluoride compound is cryolite.
5. Process according to claim 4 characterised in that the concentration of the cryolite is in the range of 5 – 30 wt%, preferably 7 – 15 wt%, more preferably about 10 wt%.
6. Process according to any of the preceding claims characterised in that the measures comprise enhancing the effective area of an anode extending into the bath by reducing the amount and/or size of gas bubbles covering the anode.
7. Process according to any of the preceding claims characterised in that the bath of molten salt mainly comprises alkali metal chlorides, preferably KCl and NaCl.
8. Process according to any of the preceding claims characterised in that the bath of molten metal is substantially free of earth alkaline chlorides.

9. Process according to any of the preceding claims characterised in that the electrolysis is carried out at a bath temperature of between 600°C and 850 °C, preferably between 700 °C and 800 °C.
- 5 10. Process according to any of the preceding claims characterised in that the electrolysis is carried out in a multi-polar electrolysis cell.

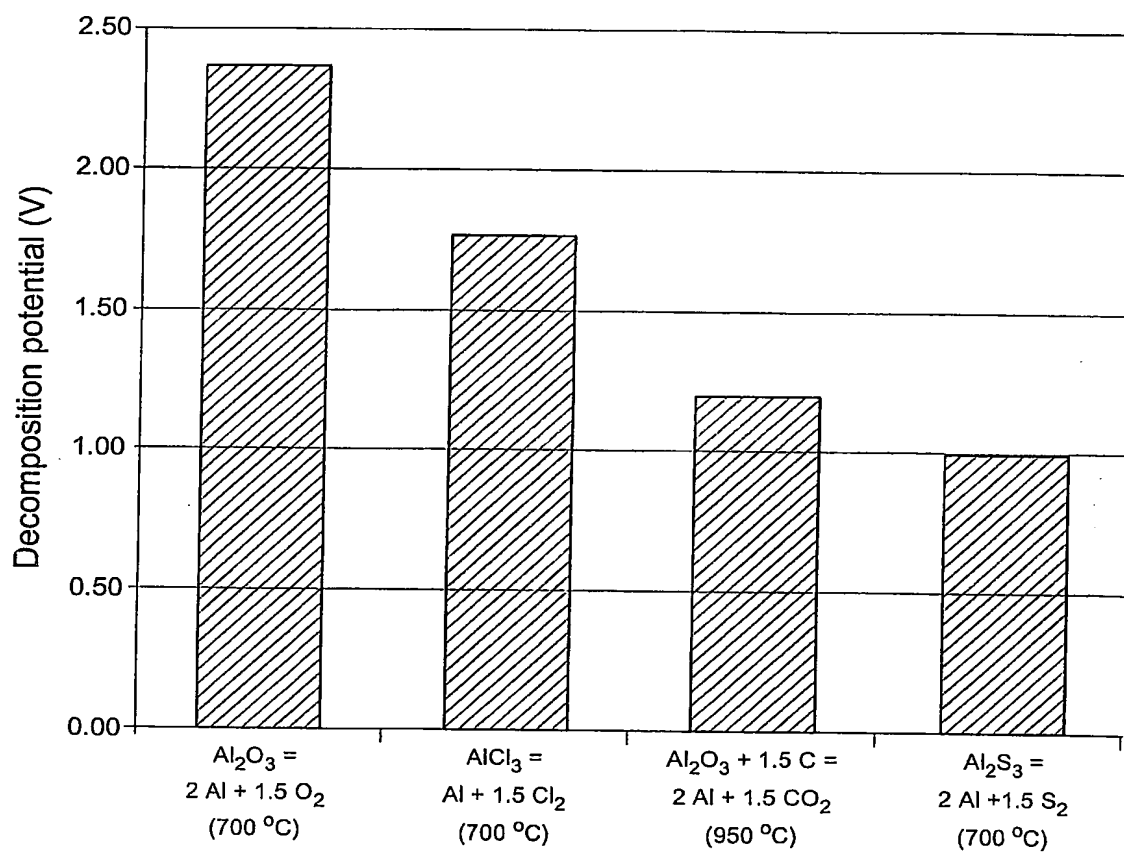


Fig. 1

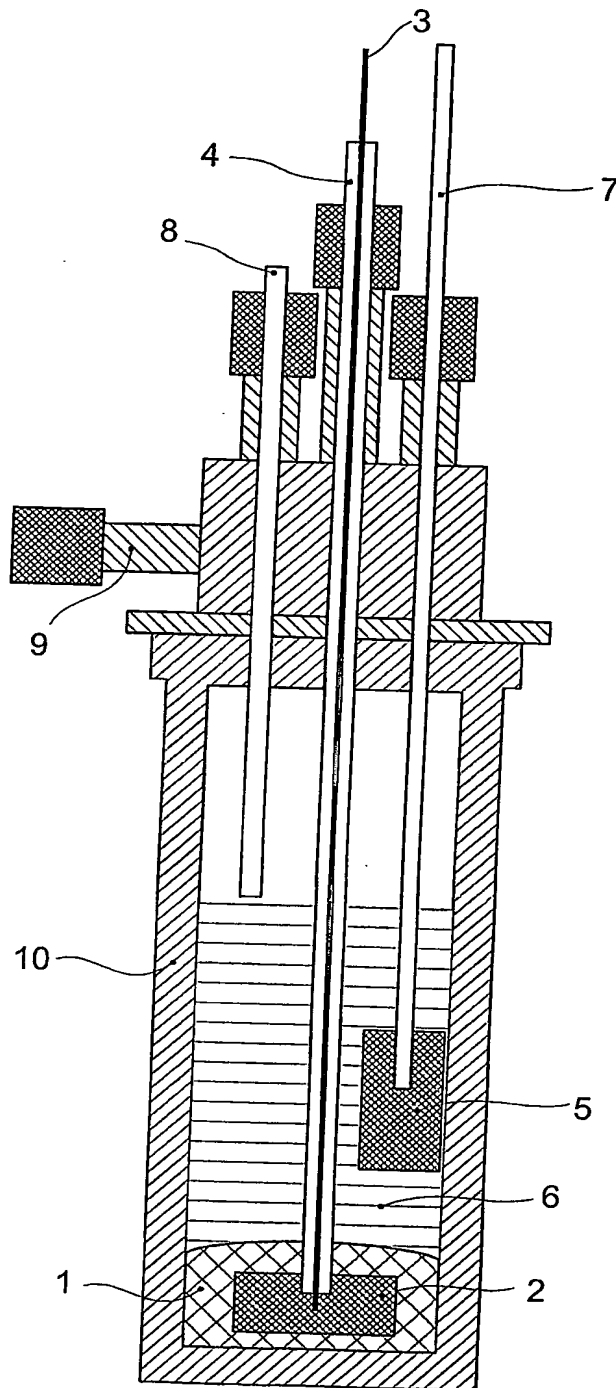


Fig. 2

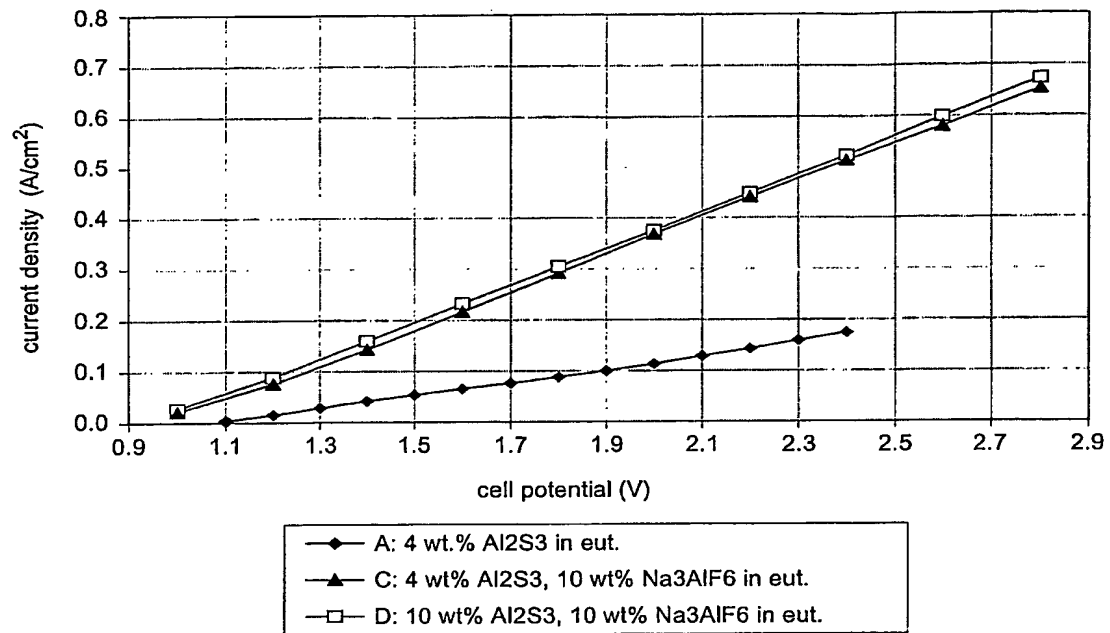


Fig. 3

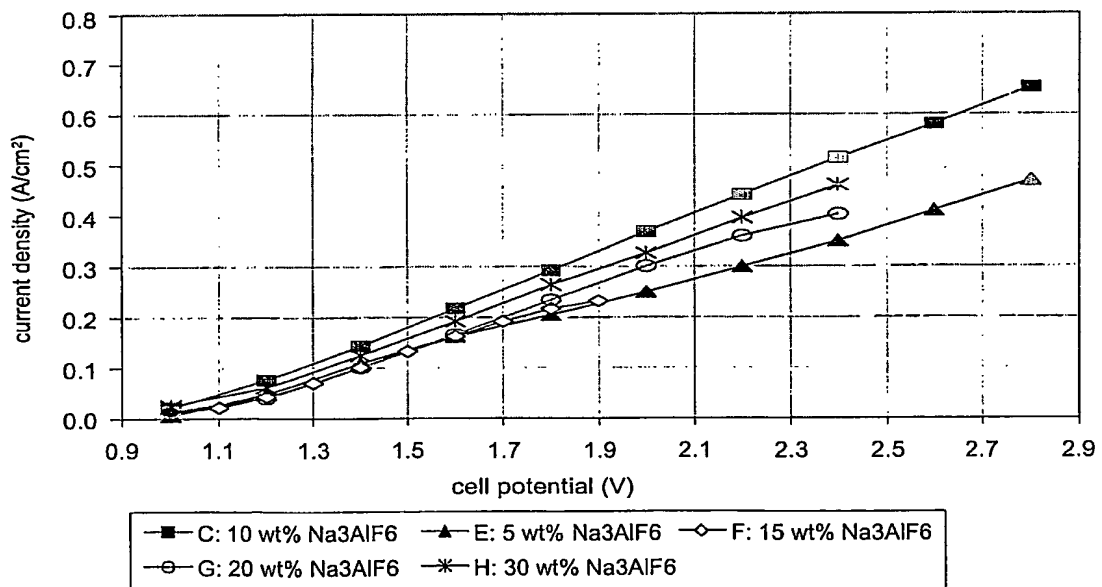


Fig. 4

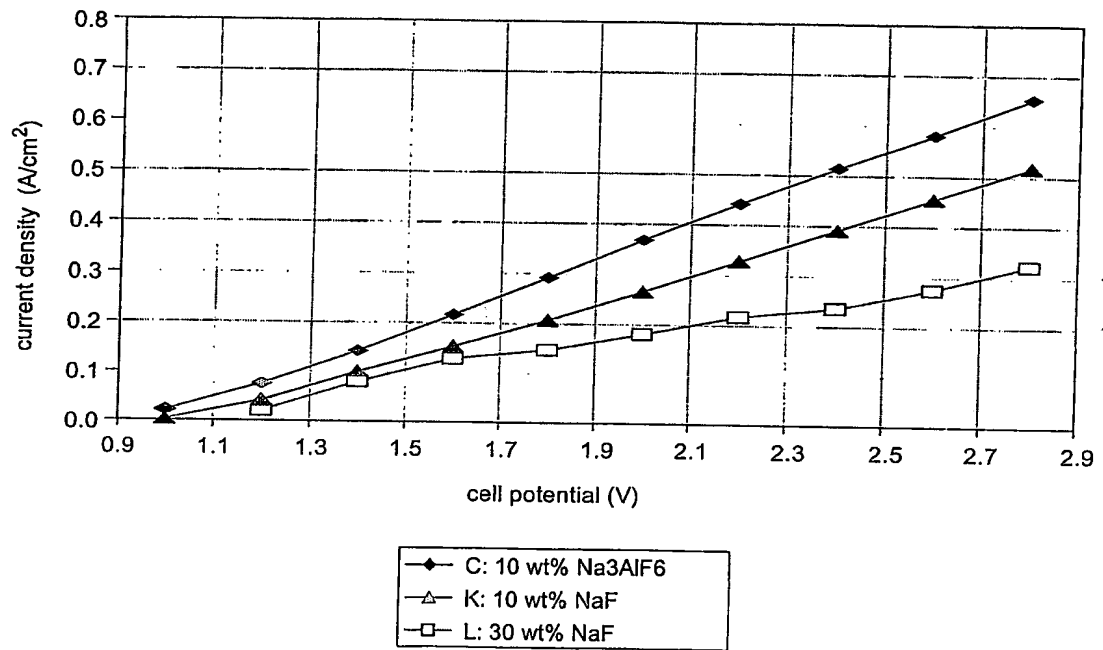


Fig. 5